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(54) **Method for the regeneration of spent alumina-based catalysts.**

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Description

The present invention relates to a method for the regeneration of spent alumina-based catalysts by removal of at least part of carbon and contaminating metal(s).

During catalytic processes wherein metal contaminated hydrocarbon feedstocks are treated with hydrogen carbonaceous matter and metals such as vanadium and nickel deposit on the catalysts, as a result of which their activities gradually decrease. When metals and carbonaceous matter are continuously deposited on the catalysts, the latter eventually have to be replaced. Substituting the deactivated catalysts with fresh batches and discarding the deactivated spent catalysts would be a costly procedure. In general it is much more attractive, if possible, to regenerate the spent catalysts and use them again for in catalytic processes.

Methods for the regeneration of spent supported catalysts are well documented in the art. It is known from British patent specification 1.526.927 that the removal of at least part of the coke from deactivated supported catalysts can suitably be performed by treating such catalysts at elevated temperature with an oxygen containing gas. An intrinsic drawback of this treatment comprises the large amount of heat evolved as a result of the exothermic oxidation of sulphur, which is present in the catalyst as metal sulphide(s). So in order to avoid the occurrence of extremely high temperatures it is necessary to remove at least part of the sulphur from the spent catalysts prior to their treatment with the oxygen-containing gas.

According to British patent specification 1.526.927 sulphur can be removed from silica-based spent catalysts, by contacting said catalysts at elevated temperatures with steam.

It is also known from British patent specification 1.526.927 that contaminating metals - in essence vanadium and nickel - can be removed from spent silica-, silica-alumina - or alumina-based catalysts by extracting the deactivated catalysts with an aqueous solution of a mineral acid.

Unexpectedly it has now been experienced that spent alumina-based catalysts - in contrast to silica-based catalysts - can hardly stand the decoking and subsequent demetallization procedures described in said British patent specification.

The alumina support appears to be liable to deterioration and the treatment with an oxygen containing gas followed by extraction with acid causes an unacceptable loss of surface area and side crushing strength.

It is therefore an object of the present invention to provide a method for the regeneration of spent alumina-based catalysts, which reactivates the spent catalysts in such a way that they can be used again for catalytic purposes, without inflicting concomittently serious damage upon one or more of the properties of the catalytically active materials which are important for catalytic applications such as surface area and crushing strength.

Surprisingly it has now been found that exposing spent alumina-based catalysts successively to a treatment with steam at elevated temperature, a treatment with an oxygen containing gas at elevated temperature and a treatment with a basic medium, results in substantially regenerated catalysts which have retained in essence their catalytic properties. Thus spent alumina-based catalysts which have been exposed to the above-mentioned three-step treatment are suitable for being used again in catalytic processes.

The present invention therefore relates to a method for the regeneration of spent alumina-based catalysts by removal of at least carbonaceous material and contaminating metal(s) under controlled conditions comprising contacting said catalysts with steam at elevated temperature, thereafter burning carbonaceous matter therefrom in the presence of an oxygen-containing gas and subsequently treating it with a basic medium.

From French patent specification 2,099,532 a process is known for regenerating aluminium oxide which has become contaminated with organic compounds in a process for producing hydrogen peroxide with the aid of a solution containing quinone and hydroquinone. The contaminated catalyst is regenerated by first treating the catalyst with water vapour and then with an alkaline solution.

Further, it should be noted that it is known from United States patent specification 4,409,190 to remove cobalt from a spent supported catalyst after carbon has been burned-off therefrom, by treating the catalyst firstly with an aqueous basic solution and secondly with an aqueous cyanide solution.

In the process according to the present invention the alumina-based spent catalysts are firstly treated at elevated temperature with steam. This steam treatment is preferably carried out at a temperature above 200 °C and in particular at a temperature in the range from 250-500 °C. As a result of the treatment of the deactivated alumina-based catalysts with steam, the subsequent treatment with an oxygen-containing gas at elevated temperature is much easier to control and requires moreover much less time.

The treatment of the deactivated alumina-based catalysts with an oxygen-containing gas at elevated temperature is preferably carried out at a temperature in the range from 300-750 °C and in particular at a

temperature in the range from 350-550 °C. Thereby it preferred to use air or a mixture of air and nitrogen as the oxygen-containing gas. The treatment with the oxygen-containing gas may be carried out directly after the treatment with steam, but also at a later moment, after the material treated has been cooled.

In the final step of the regeneration method according to the invention, the alumina-based spent catalysts are exposed to a treatment with a basic medium. Good results have been obtained by using an ammonia/ammonium buffer having a pH of 9-12. Preferably, use is made of an ammonia/ammonium carbonate buffer of pH 10. The treatment with the basic medium is preferably carried out at a temperature in the range from 5-100 °C.

If the alumina-based catalysts to be regenerated contain one or more metals with hydrogenating activity other than vanadium and nickel, such as cobalt, molybdenum or tungsten, it is likely that in the regeneration process according to the invention at least part of these metals is removed from the reactivated catalyst together with vanadium and nickel. Thus, if the regenerated catalyst is to be used in a process wherein the presence of part or all of such metals is required, an additional amount of these metals should be supplied to the regenerated catalyst to obtain their desired level. The regeneration method according to the invention is applicable for alumina-based catalysts which have become deactivated in a process wherein a metal(s)-containing hydrocarbon oil is treated with hydrogen at elevated temperature and pressure. Examples of such treating processes are hydrodesulphurization, hydrocracking and hydrodemetallization. The regeneration method according to the invention is of special importance for the regeneration of spent catalysts used in large hydroconversion processes.

The invention will now be further elucidated with the aid of the following Example.

Example

An Experiment was carried out using a spent $CoMo/Al_2O_3$ catalyst, conventionally deoiled with toluene/pentane. Its properties are given in Table 1.

Table 1

PROPERTIES OF SPENT CATALYST

composition (% w/w)	Al		42.0
	Mo		8.1
	Co		2.8
	Ni		4.0
	V		9.0
	C		13.3
	S		14.7
side crushing strength	(SCS)	(N/cm)	89
bulk crushing strength	(BCS)	(MPa)	1.2
pore volume	(PV)	(ml/g)	0.25
surface area	(SA)	(m^2/g)	104

The spent catalyst was treated with steam at 400 °C for 4h (dT/dt = 100 °C/h) in a fixed bed through which a gas flow of atmospheric pressure was led. The composition of the gas was 50/50 steam/nitrogen. After 4 hours, the steam in the nitrogen flow was slowly (in 2 hours) replaced by air maintaining a temperature of 400 °C. After the steam has been replaced by air, the material was treated in full air for

another 4 hours. Subsequently, the material was cooled and treated with an ammonia/ammonium carbonate buffer solution (pH = 10) at a temperature of 20 °C, during 18 hours. The ratio of buffer over spent catalyst was 10 ml/g. The results of this regeneration experiment are shown in Table 2.

Table 2

RESULTS REGENERATION EXPERIMENT

		(in %)
Removal of:	V	65
	Ni	90
Retention of:	Co	50
	Mo	25
	SA	100
	PV	100
	SCS	95

It will be clear from the results expressed in Table 2, that the combination of steam hydrolysis/direct decoking/treatment with a basic medium is suitable for the removal of large amounts of contaminating metals from the spent alumina-based catalyst, with substantial retention of the catalyst's surface area, pore volume and side crushing strength.

Comparative Example

A spent alumina-based catalyst having the properties as described in Table 1 was treated with an air/nitrogen mixture (50/50) during 4 hours at 400 °C (dT/dt = 100 °C/h) followed by treatment in air for another 4 hours. After this treatment the catalyst was completely desintegrated which made further regeneration impossible.

In order to achieve at least some regeneration, another batch of said alumina-based spent catalyst was treated with very diluted air under a very low heating rate (400 °C was finally reached after more than 150 hours). After cooling, the thus treated material was subjected to a treatment with 0.5 M H_2SO_4 at 20 °C for a period of 18 hours. The results of this comparative regeneration experiment are shown in Table 3.

Table 3

RESULTS COMPARATIVE EXPERIMENT

		(in %)
Removal of:	V	50
	Ni	65
Retention of:	Co	30
	Mo	40
	SCS	-*

* About 6% of the alumina-carrier was dissolved which completely destroyed the side crushing strength of the material.

It will be clear from the results expressed in this Comparative Example that the combination of direct decoking (even under mild conditions)/treatment with an acidic medium is not suitable for the regeneration of spent alumina-based catalysts.

The 3-step regeneration process according to the present invention - if desired, followed by a re-impregnation with one or more hydrogenation metals - therefore, is an attractive regeneration method for spent alumina-based catalysts.

Claims

1. Method for the regeneration of spent alumina-based catalysts by removal of at least carbonaceous matter and contaminating metal(s), under controlled conditions comprising:
   (a) contacting said catalyst with steam at elevated temperature,
   (b) thereafter, burning carbonaceous matter therefrom in the presence of an oxygen-containing gas, and
   (c) subsequently treating it with a basic medium.

2. Method according to claim 1, wherein the catalyst is contacted with steam at a temperature in the range from 200-500 °C.

3. Method according to claim 2, wherein the temperature is in the range from 300-450 °C.

4. Method according to any one of claims 1-3, wherein the carbonaceous matter is burned-off at a temperature in the range from 300-750 °C.

5. Method according to claim 4, wherein the temperature is in the range from 350-550 °C.

6. Method according to any one of claims 1-5, wherein the oxygen-containing gas is air or a mixture of air and nitrogen.

7. Method according to any one of the claims 1-6, wherein the basic medium is a buffered aqueous solution of ammonia and an ammonium salt.

8. Method according to any one of claims 1-6, wherein the basic medium has a pH of 9-12.

9. Method according to claim 7 or 8, wherein the basic medium is an ammonia/ammonium carbonate buffer of pH 10.

10. Method according to any one of claims 1-9, wherein the treatment with the basic medium is carried out at a temperature in the range from 5-100 °C.

Revendications

1. Procédé de régénération de catalyseurs usés à base d'alumine, qui consiste à éliminer au moins une matière carbonée et un ou des métaux contaminants, dans des conditions contrôlées, comprenant les étapes qui consistent :
   (a) à mettre en contact ledit catalyseur avec de la vapeur d'eau à une température élevée,
   (b) puis à en éliminer la matière carbonée par brûlage en présence d'un gaz contenant de l'oxygène, et
   (c) ensuite à le traiter avec un milieu basique.

2. Procédé selon la revendication 1, dans lequel le catalyseur est mis en contact avec de la vapeur d'eau à une température dans l'intervalle de 200-500 °C.

3. Procédé selon la revendication 2, dans lequel la température est dans l'intervalle de 300-450 °C.

4. Procédé selon l'une quelconque des revendications 1-3, dans lequel la matière carbonée est éliminée par brûlage à une température dans l'intervalle de 300-750 °C.

5. Procédé selon la revendication 4, dans lequel la température est dans l'intervalle de 350-550 °C.

6. Procédé selon l'une quelconque des revendications 1-5, dans lequel le gaz contenant de l'oxygène est de l'air ou un mélange d'air et d'azote.

7. Procédé selon l'une quelconque des revendications 1-6, dans lequel le milieu basique est une solution aqueuse tamponnée d'ammoniac et d'un sel d'ammonium.

8. Procédé selon l'une quelconque des revendications 1-6, dans lequel le milieu basique a un pH de 9-12.

9. Procédé selon la revendication 7 ou 8, dans lequel le milieu basique est un tampon ammoniac/carbonate d'ammonium de pH 10.

10. Procédé selon l'une quelconque des revendications 1-9, dans lequel le traitement avec le milieu basique est réalisé à une température dans l'intervalle de 5-100 °C.

Patentansprüche

1. Verfahren zur Regenerierung von Aluminiumoxid enthaltenden, verbrauchten Katalysatoren durch Entfernen von zumindest kohlenstoffhaltigem Material und Verunreinigungsmetall(en) unter kontrollierten Bedingungen, welches die folgenden Schritte umfaßt:
   (a) Kontaktieren des genannten Katalysators mit Dampf bei erhöhter Temperatur,
   (b) anschließendes Ausbrennen des kohlenstoffhaltigen Materials aus dem Katalysator in Gegenwart eines sauerstoffhaltigen Gases, und
   (c) anschließendes Behandeln desselben mit einem basischen Medium.

2. Verfahren nach Anspruch 1, in welchem der Katalysator mit Dampf bei einer Temperatur im Bereich von 200 bis 500 °C kontaktiert wird.

3. Verfahren nach Anspruch 2, in welchem die Temperatur im Bereich von 300 bis 450 °C liegt.

4. Verfahren nach einem der Ansprüche 1 bis 3, in welchem das kohlenstoffhaltige Material bei einer Temperatur im Bereich von 300 bis 750 ° ausgebrannt wird.

5. Verfahren nach Anspruch 4, in welchem die Temperatur im Bereich von 350 bis 550 °C liegt.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem das sauerstoffhaltige Gas Luft oder eine Mischung aus Luft und Stickstoff ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, in welchem das basische Medium eine gepufferte wäßrige Lösung von Ammoniak und einem Ammoniumsalz ist.

8. Verfahren nach einem der Ansprüche 1 bis 6, in welchem das basische Medium einen pH-Wert von 9 bis 12 aufweist.

9. Verfahren nach Anspruch 7 oder 8, in welchem das basische Medium ein Ammoniak/Ammoniumcarbonat-Puffer mit einem pH-Wert von 10 ist.

10. Verfahren nach einem der Ansprüche 1 bis 9, in welchem die Behandlung mit dem basischem Medium bei einer Temperatur im Bereich von 5 bis 100 °C durchgeführt wird.